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STRESS-CORROSION CRACKING OF AUSTENITIC
STAINLESS STEELS: AN EXAMINATION INTO
PROGRESS DURING THE PAST FIFTEEN YEARS

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Naval Research Laboratory
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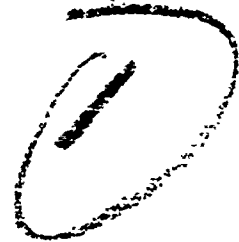
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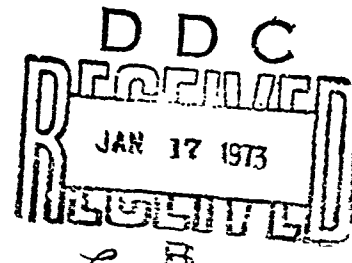


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METALLURGY DIVISION

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ABSTRACT

The literature on the subject problem was reviewed in order to trace the progress which has been made during the 15-year period and in order to identify, as far as possible, the approaches which have been useful to both the fundamental and the applied aspects of the problem. Although a completely immune steel has not been produced, as far as is known, much practical progress has been made in avoiding the incidence of stress corrosion cracking of austenitic stainless steels, but we are a long way from a full understanding of the fundamentals involved.

PROBLEM STATUS

This concludes one phase of a review of metallurgical problems being conducted for the purpose of guiding research management. Similar reviews of other problem areas are scheduled. Work on other phases of the problem is continuing.

AUTHORIZATION

NRL Problem Number M01-12

Bureau Project Number RR 007-01-46-5411

INTRODUCTION

The use of austenitic stainless steels increased greatly during the 1940's and 1950's, particularly in high pressure steam boilers, and nuclear power plants, and processing equipment for the chemical industry. In all three of these classes of applications there were instances of stress corrosion cracking (SCC*). Because of the flaw-tolerance characteristics of the austenitic stainless steels, SCC failures in components made of these do not have the spectacular finale sometimes seen in components made of martensitic stainless steels, such as rocket motor cases, in which a small stress-corrosion crack can cause the case to shatter like glass in a hydrostatic test. SCC failures, then, are unspectacular, but they can be very expensive, and they can and have closed down power plants. Thus the subject was deemed suitable for an enquiry to be made in order (1) to summarize the advances which have been made in the problem of direct usefulness to the user, (2) to summarize the advances in understanding the fundamentals of the problem even where these advances have not yet been of benefit to the user, and (3) to attempt to identify the type or types of effort which have been most fruitful in making both categories of advances. In making this enquiry, the standard English-language journals, the symposia, and selected papers in French, German, Swedish, Russian and Japanese journals were read or re-read, commencing with the year 1947.

It should be emphasized that the study was confined to the steels which are essentially completely austenitic. Moreover, with one exception the corrodents were only aqueous solutions (or vapors over aqueous solutions),

No attempt will be made here to review the details of either the theory of SCC (insofar as it has been developed) or the practical aspects of it. The reader who feels a need for either

* "Stress corrosion cracking" will be used here in the sense generally employed by the Cambridge University "School", that is, a cracking phenomenon necessarily including a stress-induced electro-chemical dissolution process. The present authors see no real benefit to be gained at this stage in trying to force this into a common framework with the only superficially related phenomena of cracking by liquid metals, purely mechanical fracture, and hydrogen embrittlement cracking.

of these is referred to Ref. 1 for the first and Ref. 2 for the latter.

PROGRESS FOR THE USER

Obviously the user would like to see the achievement of a stainless steel which can be commercially produced and fabricated and which will have properties comparable with the steels of today but which would be immune to SCC under all reasonable conditions. Failing this, he would like to know the effects (singly and in combination) of as many factors influencing cracking behavior as he can have control over for a given application.

In considering immunity to SCC one must recognize that there is no positive test capable of demonstrating this quality at present and little prospect for one in the near future: One can only report "no cracking" for the conditions and duration of his severest and longest test. There is at present no agreement on any standard test, nor any early prospect for this, either. The nearest thing to a standard test solution is boiling 42% MgCl_2 , and although external loading in tension is probably preferred by most if not all investigators, this often gives way because of cost and space to self-stressed specimens of the bent beam variety or some variant thereof. The reason that MgCl_2 is the leading contender for a "standard" corrodent is not because it is industrially important (it isn't) but apparently because many workers in the field assume it is at least among the most vicious cracking agents and additionally because it has the advantage of being able to be handled in glass apparatus. There are not enough systematic data to know whether even the order of merit of alloys in this corrodent is the same as that in other corrodents, but there are at present no discernible grounds for rejecting MgCl_2 in favor of another reagent, if one is to single out a single corrodent for evaluating progress in research and development.

It has been amply demonstrated, during the period reviewed, that no commercial austenitic stainless steel is immune to SCC, even if one restricts the consideration to MgCl_2 experiments alone, and thus the ultimate goal of the user has not been attained. This unhappy fact must have come as a painful surprise to many users who perhaps assumed that the "stabilized" steels (containing niobium or titanium), particularly those with extra low carbon which thereby commanded a price premium, would be immune to cracking; but it is now rather generally realized that one simply cannot buy the immunity in the steel and that the nearest approach to practical immunity requires the summing of all possible partial solutions to the problem, as discussed below.

It will become apparent in reviewing the progress in understanding the effects of various factors, which represent what is being termed partial solutions, that in the aggregate considerable progress of immediate value to the user has been made, even though the ultimate solution is still unattained.

A. Effect of temperature. The temperature coefficient of the overall cracking process has been measured with varying degrees of rigor for various combinations of steels and corrodents. In all cases measured the temperature coefficient is appreciable, but it varies considerably depending upon the combination. As an example of the magnitude that may be found, it is observed that a decrease of about 15 centigrade degrees slows the time to fracture steel of approximately the 304 type in 42% $MgCl_2$ by a factor of ten. This high temperature coefficient doubtless accounts for the fact that a steel such as Type 304, which is highly susceptible to cracking in $MgCl_2$ at about 150°C, serves so well at or near room temperature. A high coefficient also doubtless accounts for the fact that a corrodent as mild as dilute NaCl cracks a given steel faster at 250°C than $MgCl_2$ at 150°C. This does not mean that the austenitic stainless steels will not crack at room temperature - indeed several room temperature failures are reported in Ref. 2, in such media as aqueous NH_4Cl and even the soaps and greases used as die lubricants, but room temperature incidence is comparatively very rare. As a corollary of this, we may in the future observe cracking in components which have performed perfectly satisfactorily at somewhat lower temperatures.

B. Effect of stress. The development of a definitive statement on the effect of stress on cracking has been hampered by the fact that in some steels some corrodents (such as hot nitric acid, for example) cause intergranular cracking in the absence of stress. There are several reasons to consider such cracking as belonging in a fundamentally different category from the cracking which is the subject of the present study. Many authors clearly recognize this, and the term "intergranular corrosion" is frequently employed to designate this category. Failure to recognize this difference accounts for the mistaken assumption that lowering the carbon content would reduce susceptibility of SCC.

Restricting the subject then to the cracking which requires some appreciable stress, it is observed (using boiling $MgCl_2$ solutions) that below a certain stress level for a given steel the cracking time increases so rapidly with decreasing stress

that for many practical purposes one might consider that cracking does not occur. This stress level varies from roughly 5,000 psi for the most susceptible types (e.g., 304) to perhaps 40,000 psi for the most resistant types (e.g., 310).

C. Effect of thermal and mechanical treatments. Fit up stresses in large or complex structures or components and residual stresses from welding may easily exceed the 5,000 - 40,000 psi figures cited above. Hence it has been found beneficial to heat treat structures or components after fabrication, where possible.

Stress corrosion cracking has not been observed under compressive stresses. One might conclude from this that shot-peening, which tends to leave the surface in compression, might be effective in mitigating SCC. This has in fact been observed for both austenitic stainless steels and a martensitic stainless steel. It is somewhat surprising, particularly in view of the state of development and of shot-peening technology and equipment, that more studies on the effectiveness of this treatment on SCC have not been reported. The point has been made that in some cases the surface may already be in compression and that in such cases shot peening may relieve some of the compressive stresses and thereby worsening matters rather than improving them.

D. Effect of steel composition. During the fifteen year period there was published a rationale of the SCC of homogeneous alloys which gave little hope for finding immunity in steels of low (e.g., 8%) Ni content. Actually, findings in Germany during WW II had indicated an important benefit from increasing nickel content, and during the fifteen year period under review this was fully confirmed, the indications being that the nickel content might have to be of the order of 50% for immunity. Addition of Ni to a Fe-Cr alloy decreases the time for cracking as Ni content is increased, reaching a minimum in holding time at about eight percent Ni, after which the holding time increases with further additions of Ni, and the alloy appears to become immune at compositions containing Ni contents of about 50 percent or more. (It should be noted however that recently a high Ni containing alloy (Alloy I*) has been reported to crack in 350°C water).

* A proprietary alloy containing approximately 79.5% Ni, 13% Cr, and 6.5% Fe.

In wholly austenitic stainless steels nitrogen was shown to be highly detrimental, but carbon was shown to be beneficial (as discussed earlier). Molybdenum appears to be somewhat detrimental. The other elements studied either have little or no effects, or the effects have been in different directions in different studies.

E. Effect of microstructure. The appearance of ferrite in an otherwise austenitic alloy tends to inhibit cracking; the presence of martensite, on the other hand, appears to promote cracking, perhaps by purely mechanical effects.

F. Effect of corrodent composition. Many of the studies on corrodent composition have been carried out in boiling solutions, and the results are not always readily interpretable because of temperature differences which may either swamp or exaggerate the intrinsic effect of composition. Furthermore, the question of the possible effects of the last traces of contaminants is, for the purist, unanswered. For practical purposes, however, either a halide or caustic must be present, but free oxygen is not required in the case of caustic solutions. Of the halides, chlorides, fluorides and bromides have been observed to cause cracking. Solutions of $MgCl_2$, which are slightly acid, are more aggressive than those of $NaCl$, which are neutral; and the addition of HCl to $MgCl_2$ speeds cracking, but the addition of $NaOH$ slows it. Furthermore, specimens exposed in both boiling aqueous $MgCl_2$ and the vapor space above it are observed frequently to break in the vapor space (which contains HCl in addition to water vapor) sooner than in the liquid. The concentration of chemicals needs not be high to cause cracking if the temperature is high: rapid cracking has been reported in $NaCl$ solutions well below 1% and without added acid, but pressurized so that the test could be conducted at $250^{\circ}C$. The threshold concentration of chloride ion necessary for cracking appears to decrease with increase in temperature.

G. Inhibitors. Inhibitors such as disodium phosphate and reducing agents have been added to corrodents, but they have been only indifferently successful in combatting SCC, and outlook for such a solution to the problem is unpromising.

H. Cathodic protection. Numerous studies have shown that cathodic protection where feasible, is effective in preventing cracking. Polarization of as little as 50 millivolts was observed to confer apparent immunity. Unfortunately, however, in many applications the bulk of the solution may be of very high resistance (as in pressurized water reactors) or the

corrodent may exist only as a thin film, as in a superheater tube during dry-out, and cathodic protection schemes would of course not be feasible under these circumstances.

PROGRESS IN THEORY (NOT YET TO STAGE OF BEING OF PRACTICAL USEFULNESS)

The effectiveness of cathodic protection in preventing SCC, or to arrest cracking already in progress when the cathodic protection is applied, indicates that the phenomenon of SCC necessarily involves an electrochemical process, presumably the anodic dissolution of metal at the advancing edge of the crack. Since stress strongly affects cracking kinetics, it presumably influences the electrochemistry; the effect of stress on the standard electrode potentials appears to be far too small to be responsible, but strain-induced depolarization of anodic areas under continuous yielding has been shown to be of significant magnitude. It has been postulated that the overall cracking process includes not only the electrochemical step discussed above but also a periodic fracture step of purely mechanical nature, but the evidence is incomplete for this. A hypothesis has also been put forth that wedging action produced by deposition of solid corrosion products in cracks develops lateral tensile forces which when combined with residual and applied stresses present yield forces of sufficient magnitude to trigger spontaneous crack propagation. It has been postulated that SCC does not occur in crystals which can exhibit easy cross slip. It has been observed (in copper-based alloys in the form of foil being electrochemically thinned for transmission electron microscopy) that corrosion tended to take place preferentially along crystallographic stacking faults where these are of low energy, but not where they were of high energy. Sensitivity to cracking has also been related with ability to form corrosion products of unusual crystal habit.

This is a highly condensed summary of ideas and observations relating to theory which the interested reader may wish to see discussed in fuller detail, as in Ref. 1. The fact that all of these are in this section of the report and not in the listing of "partial solutions" for the user is because even if any or all of them should be proven correct, we do not at the present time know how to make use of them to prevent SCC.

APPROACHES TO PROGRESS

It is clear that the approach which has been most productive from the standpoint of the user has been one of systematic, careful testing on a large scale, and that such testing has

brought real progress during the fifteen-year review period. There seems to be no reason to be confident of a change in this situation in the near future. It is not clear, because of the confused state of the theory, just which approaches are most likely to be beneficial in clarifying the fundamentals involved, but it seems unlikely that any approach can move the theory along very far unless it includes a sophisticated comprehension of both applied electrochemistry and crystal mechanics. Even with further development in the theoretical aspects, it is not very likely that any single theory of stress corrosion cracking will be found to be applicable to all combinations of metals and corrodents.

OUTLOOK

No basis can be seen for confidence that theory can overtake, much less pass, empirical alloy development to mitigate SCC in the near future. This in no way can be taken as grounds to de-emphasize fundamental work on the problem: The more fundamentals we really know, the easier it is in a complex technological world to reduce empirical findings to a more readily assimilated form. But there does not appear to be any good reason to delude oneself with the notion that a few more experiments will yield a theory from which we will design improved alloys in this field.

Sufficient advances have been made in empirical alloy development in the very recent past to feel optimistic that a nearly immune alloy, if not one entirely immune, may yet be attained. The finding that high purity steels of the general class 16% Cr - 20% Ni, which is not grossly different from some of our commercial compositions, is not cracked in acidified $MgCl_2$, or in $MgCl_2$ in which the alloy is made an anode, supports this view. Actually much more testing needs to be done on the 16 Cr - 20 Ni alloy before it can be called immune to stress corrosion cracking. Such testing should include longer tests at higher temperatures using different corrodents and different stress levels, using notched and unnotched specimens and comparing the results with those obtained using a commercial austenitic stainless steel. It would require a substantial program, however, to explore how far one can depart from the high purity alloy toward a commercial composition and still retain resistance to cracking in various corrodents. The non-catastrophic nature of most SCC in austenitic steels, the advances in "partial solutions", and the existence of alloys containing very high nickel which are largely immune to cracking in various corrodents, would seem to greatly increase the difficulty of making a case for a large program in this problem area at this time.

REFERENCES

1. S. Barnartt, Corrosion 18, 322t (1962), (85 references)
2. Report on Stress Corrosion Cracking of Austenitic Chromium-Nickel Stainless Steels, ASTM Special Technical Publication No. 264 (1960), (245 references)